

# In-situ hybrid study of thermal behaviour of Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> nanocrystallite thin films induced TEA/MEA by electrocodeposition



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## ABSTRACT

Our present investigation focuses on the thermal stability of already developed electroforms of Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> thin films induced with triethylamine (TEA) and monoethylamine (MEA) as surfactant by electrocodeposition on mild steel substrate with the aim to re-examine its micro-hardness and degradation behaviour in static sodium chloride solution. In the event, the samples were thermally treated at 200 °C and air cooled. The results obtained showed that the developed composites are thermally stable with hardness value of the Zn–Ni–Al<sub>2</sub>O<sub>3</sub> coated; 185 Hv increased to 190.5 Hv indicating a 2.89% improvement. Noticeably, in the Zn–Ni coatings, a decrease in the hardness with 26.67% was observed. The oxidation resistance was however favored for both composites.

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## Introduction

Steel and its alloy group have wide range of application due to the high strength, availability, ease of fabrication, low cost among others [1–4]. In most service condition, there exist limitations as per the hardness and corrosion resistant of using this important alloy. Accordingly, various techniques have been put forward as a means of enhancing its properties [1,5,6]. In that direction, surface treatment has long time gained acceptance as a method of simultaneously improving the alloy hardness and corrosion/oxidation resistance. Among these surface treatment techniques, the use of electrocodeposition for surface coating has been promising due to advantages it has over other; such as wear resistance, self-lubricating, corrosion or oxidation resistance [6,7]. In an event to examine the thermal stability of our earlier developed Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> films on mild steel [8,9], effort was made to heat treat the coated composite and then re-examine its micro-hardness and corrosion resistance in the thermally treated condition. The present study is aimed at evaluating the micro-hardness and corrosion of isothermally treated Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> thin films induced TEA/MEA by electrocodeposition on mild steel substrate.

## Experimental method

The dimension of the mild steel (substrate) used was 40 mm × 20 mm × 1 mm sheet and zinc sheets of 30 mm × 20 mm × 1 mm were prepared as anodes. The mild steel specimens' chemical composition is shown in Table 1. The bath constituent admixture, other plating parameters and optimum results were adopted from our previous study [8].

For isothermal treatment of the Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> coated composite, the coated composite sample that gave the best hardness in [7,8] were re-examined after thermal treatment. The electroform of coated Zn–Ni–mild steel and Zn–Ni–Al<sub>2</sub>O<sub>3</sub>–mild steel were heat treated at a temperature of 200 °C for 2 h in an electrical heating furnace under atmospheric conditions and then quenched in air.

Vickers micro-hardness tester under a load of 100 g and a spacing of 150 μm with a dwell time of 15 s with an average of four measurements from different locations was used to evaluate the hardness of the as-deposited and thermally treated (heat treated) composite using a hardness tester with model-Dua scan inventor-EMCOTEST. The indentations started at the surface of the coated-body through the base of the mild steel substrate. The electrochemical studies were done with Autolab PGSTAT 101 Metrohm potentiostat using a three-electrode cell assembly in a 3.65% NaCl static solution at 40 °C. The heat treated composite was the working electrode, platinum electrode was used as counter

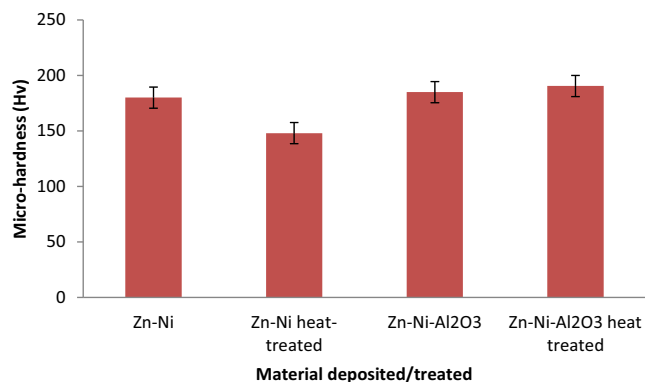
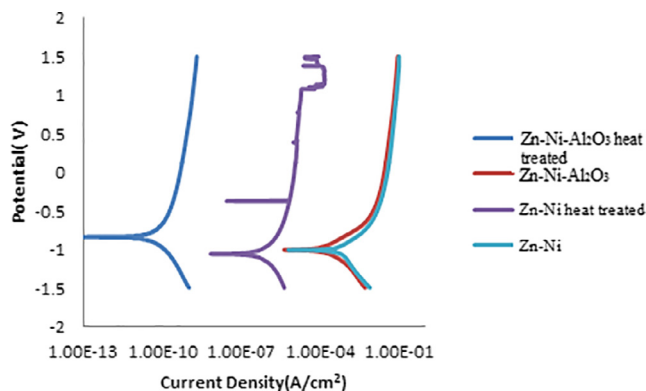
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**Table 1**

Chemical composition of mild steel used (wt%).

Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

**Fig. 1.** Variation of micro-hardness for the as-deposited and heat-treated conditions.**Fig. 2.** Linear polarization curve for the as-deposited and heat treated conditions.**Table 2**

Polarization data for the untreated and thermally treated composite sample in a static 3.65% NaCl solution.

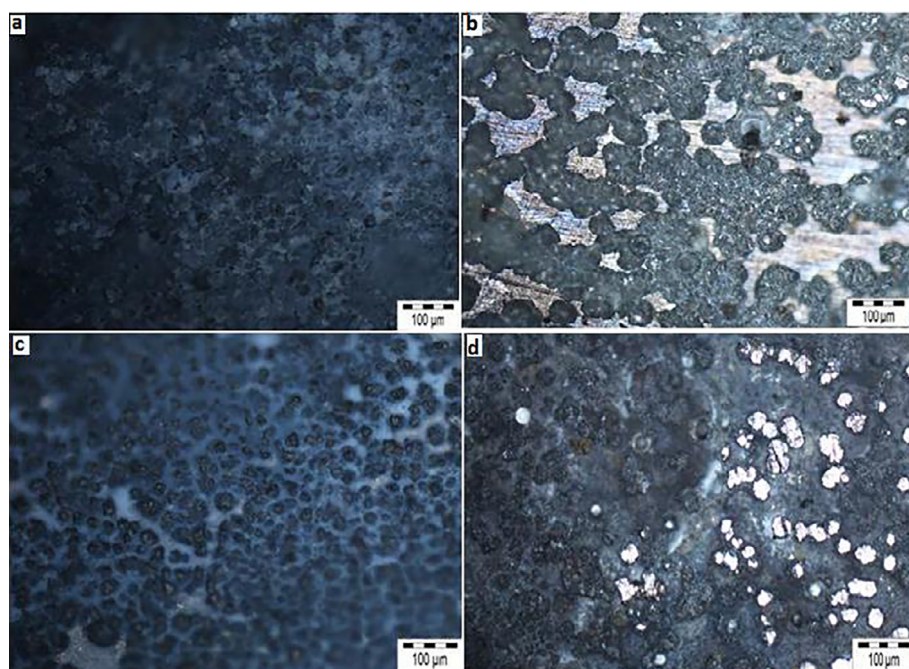
Samples	Ecorr, Obs (V)	jcorr (A/cm <sup>2</sup> )	icorr (A)	CR (mm/yr)	Rp(Ω)
Zn–Ni	–1.0665	5.43E–05	5.43E–05	6.31E–01	435.91
Zn–Ni Heat treated	–1.0622	7.13E–08	7.13E–08	8.28E–04	154
Zn–Ni–Al <sub>2</sub> O <sub>3</sub>	–1.0103	4.70E–05	4.70E–05	5.47E–01	221.57
Zn–Ni–Al <sub>2</sub> O <sub>3</sub> Heat treated	–0.8460	5.57E–12	5.57E–12	6.48E–08	2224

electrode and Ag/AgCl as a reference electrode. The anodic and cathodic polarization curves were recorded by a constant scan rate of 0.012 V/s which was fixed at  $\pm 1.5$  mV. From the Tafel extrapolation plots, the corrosion rate, potential and linear polarization resistance was obtained.

## Results and discussion

The results obtained showed that the developed composites are thermally stable with hardness value of the Zn–Ni–Al<sub>2</sub>O<sub>3</sub> coated; 185 Hv increased to 190.5 Hv indicating a 2.89% improvement (see Fig. 1). The reason for this observation is still unclear, though the ceramics phases likely formed might be responsible, such that at high temperature the oxide layer became hardened and resistance to any external forces. However, this may scale-off over a prolong period of post heat treatment time. Although in the Zn–Ni coatings, a decrease of about 26.67% in the hardness was observed. This demonstrated that the addition of Al<sub>2</sub>O<sub>3</sub> particles in the Zn–Ni matrix improves its thermal stability by acting as a barrier to dislocation motion and hence reducing the grain growth. Similar claim was reported [9]. Relatively, an increased micro-hardness of heat treated Zn–Ni–Al<sub>2</sub>O<sub>3</sub> coating can be attributed to the ceramics particle inoculated. Similar occurrence has been reported [10].

The polarization resistance of Zn–Ni coated decreased from that of as-deposited to heat treated sample. While that of heat

**Fig. 3.** Surface optical microstructure of as-coated composite for (a) Zn–Ni (b) Zn–Ni heat treated (c) Zn–Ni–Al<sub>2</sub>O<sub>3</sub> (d) Zn–Ni–Al<sub>2</sub>O<sub>3</sub> heat treated.

treated Zn–Ni–Al<sub>2</sub>O<sub>3</sub> increased with respect to as-deposited Zn–Ni–Al<sub>2</sub>O<sub>3</sub> (Table 2). The oxidation resistance was however favored for both composites (see Fig. 2 and Table 2). Accordingly, the surface morphology of the samples generally indicated an oxidized surface (Fig. 3a–d). This however calls for further investigation since it is expected that such surfaces may likely have contained un-adhered film coating at that temperature. Considerably, such suggest that the film formed on the mild steel substrate are thermally stable and hence indicates good bath admixture during the electrocodeposition of the coatings.

## Conclusions

The thermal stability of already developed Zn–Ni and Zn–Ni–Al<sub>2</sub>O<sub>3</sub> thin films induced TEA/MEA by electrocodeposition was evaluated with the aim to re-examine its micro-hardness and degradation behaviour in static sodium chloride solution. In the event, the samples were thermally treated at 200 °C and air cooled. The results obtained showed that the developed composites are thermally stable with hardness value of the Zn–Ni–Al<sub>2</sub>O<sub>3</sub> coated; 185 Hv increased to 190.5 Hv indicating a 2.89% improvement. Although in the Zn–Ni coatings, a decreased hardness was observed, while the oxidation resistance was rather favored for both composites.

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## Further reading

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